The Second Law

- The *entropy change* for a system is the change in heat absorbed during a reversible process divided by the temperature of that change.

$$\Delta S = \int \frac{dq_{rev}}{T}$$

- Formally, the *second law of thermodynamics* states that for any change the total entropy change is greater than or equal to zero:

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} \geq 0\text{, or } \Delta S_{tot} \geq \int \frac{dq}{T}$$

The Second Law

- Alternative statements:

$$\Delta S_{sys} \geq \int \frac{dq_{irrev}}{T}$$

"Heat cannot be spontaneously transferred from a cold object to a hot object."

"Entropy must increase or remain constant in an isolated system."

"You can't create a perpetual motion machine."

Standard State Entropies

- Same idea as enthalpies: define a standard state and operate relative to that

$$\Delta S^0 = S_{obs} - S_{ref}$$

- Any property of ΔS is a property of ΔS^0 (or $\Delta \bar{S}^0$):

$$\Delta S^0(T_2) - \Delta S^0(T_1) = C_P \ln\left(\frac{T_2}{T_1}\right)$$

- Reference state for entropy is S at 0 K (more on that later)

Summary: Entropy Changes

- Temperature (also true for C_V at const. V)

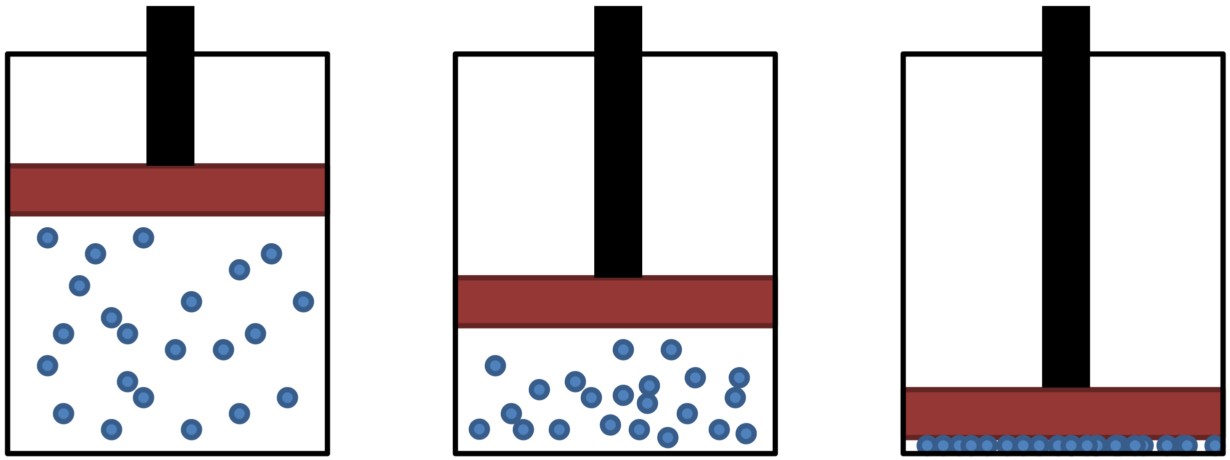
$$S(T_2) - S(T_1) = C_P \ln\left(\frac{T_2}{T_1}\right)$$

- Phase Change

$$\Delta S_{tr}(T_{tr}) = \frac{\Delta H_{tr}(T_{tr})}{T_{tr}}$$

- Pressure Change
  - Approximately zero for solids, liquids
  - Ideal gasses at constant T: $\Delta S = -nR\ln\left(\frac{P_2}{P_1}\right) = nR\ln\left(\frac{V_2}{V_1}\right)$

Molecular Interpretation of Entropy



Many configurations for gas molecules Fewer configurations for gas molecules

- *Entropy is a measure of the number of microscopic configurations a system can have while maintaining the same macroscopic properties (volume, temp., density, etc.)*

Predicting Entropic Changes

- Using concept of disorder, we can often predict sign of entropy

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$

$$\Delta\bar{S}^0 = 89 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

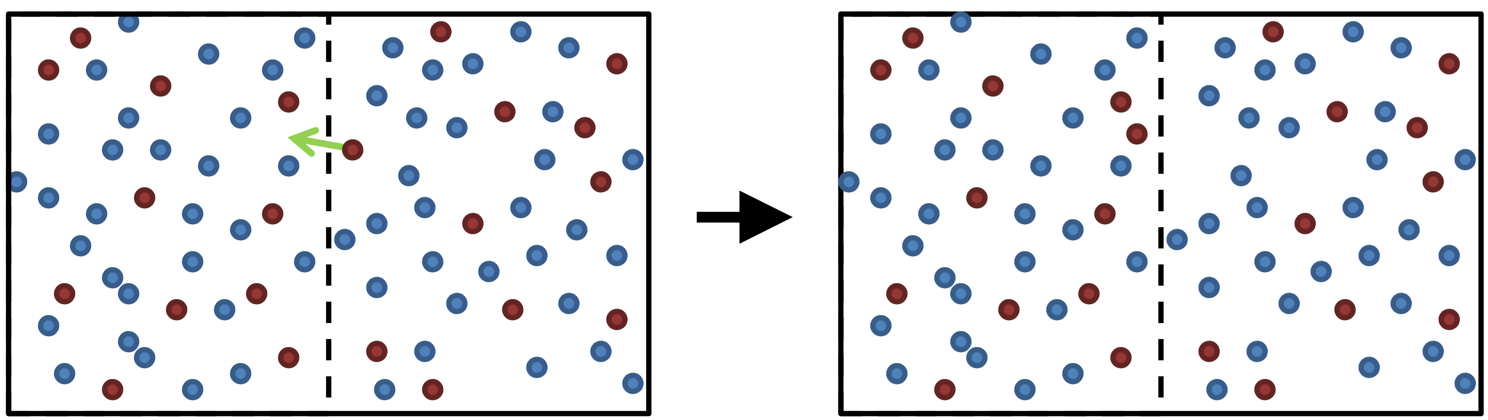
- Hard to predict total changes in aqueous solution (system + surroundings) because water can become ordered or disordered

$$NH_4^+(aq) \rightarrow H^+(aq) + NH_3(aq)$$

$$\Delta\bar{S}^0 = -2 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

Is the Second Law Always True?

- Consider a microscopic fluctuation, caused by random (Brownian) motion:



- The red molecules are no longer evenly distributed

Introduction: Gibbs Energy

- **Recall:** Any combination of state variables is also a state variable

$$G \equiv H - TS = E + PV - TS$$

- Any change in G can be represented as before:

$$\Delta G = \Delta H - \Delta(TS)$$

- Additionally, let's no longer assume only P, V work:

$$dw = -P_{ex}\Delta V + dw_{rev}^{*}$$

Implications: ΔG at const. T, P

- In a chemical reaction, some work is required to change volume a small amount
  - This is not *useful* work to a chemist

- ΔG is the (useful) work done *by* the system for a given process
  - The inverse, $-\Delta G$ is the maximum amount of useful work the system can do on the surroundings
  - Irreversible work is not as efficient

Implications: ΔG at const. T, P

- If ΔG = 0 for a process:
  - System can do no (non-PV) work on surroundings
  - Equilibrium state
- If ΔG > 0 for a process:
  - Work done by surroundings is negative; work is required to complete process
  - Process it not spontaneous (it needs work)
- If ΔG < 0 for a process:
  - Work done on surroundings is positive ($-dw^*_{rev} > 0$)
  - Process occurs spontaneously (no work needed)

Implications: ΔG at const. T, P

- If we know ΔH and ΔS for any process at constant T, P (or ΔH^0 and ΔS^0)

$$\Delta G = \Delta H - T\Delta S$$

and

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

- Follows directly from the definition of G